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# Surface modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microsphere by silane coupling agent

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## Abstract

In the present study,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell microspheres were prepared via two steps. First,  $\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by co-precipitation of  $\text{Fe}^{+3}$  and  $\text{Fe}^{+2}$  as reaction substrates and NaOH as precipitant. Second, the surface of  $\text{Fe}_3\text{O}_4$  was coated with silica by hydrolysis of tetraethylorthosilicate as the silica source. Subsequently, in order to reduce the amount of interaction and the agglomeration of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres, the silica shell of these particles was modified by vinyltriethoxysilane as the silane coupling agent. The structural properties of the samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Fourier transform infrared spectroscopy analyses. The results indicated that the average sizes of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles were about 50 and 500 nm, respectively. Also, the surface characterization of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres showed that the silane coupling agent was covalently coupled with the silica surface.

**Keywords:** Agglomeration, Co-precipitation, Coupling agent,  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  core-shell microsphere

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## Background

Magnetic microspheres and magnetic core-shell structures are highly applied in bio and environmental researches [1-3]. Magnetic microspheres, consisting of an iron oxide core and a silica shell, have attracted more attention for their unique magnetic responsivity, low cytotoxicity, good stability, and chemically modifiable surface [4-7]. The core-shell magnetic silica microspheres have shown good potential for different applications, including bioseparation, enzyme immobilization, and catalysis [8-11].

There are various ways to prepare  $\text{Fe}_3\text{O}_4$  nanoparticles, which have been reported in several papers, such as arc discharge, mechanical grinding, laser ablation, microemulsions, high temperature decomposition of organic precursors, etc. [12]. As a simple and cheap method, chemical co-precipitation has the potential to meet the increasing demand for direct preparation of well-dispersed (water-based)  $\text{Fe}_3\text{O}_4$  nanoparticles, and it offers a low-temperature alternative to conventional powder synthesis techniques in the production of nanoparticles. Also, through this method,

the sizes of nanoparticles can be well controlled by apt surfactant [13,14].

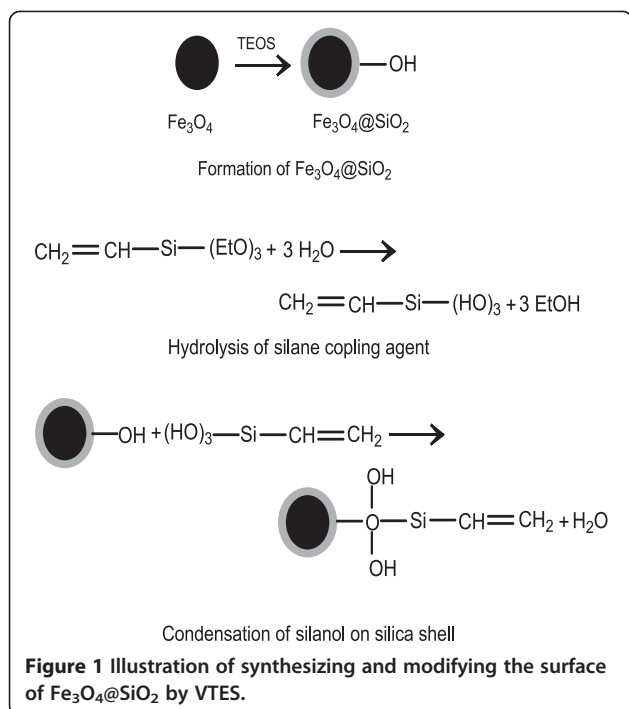
Surface coating is one of the methods which have often been used in modifying or in improving the material's performances [15]. There are several promising techniques for coating the surface of particles; most of them are chemical processes, such as precipitation, sol-gel, and electrochemistry methods. The heterogeneous nucleation method is usually used in surface coating because of its simple procedure, low cost, and especially, easy controlling of the thickness and composition of the coating layer [16]. The proper shell thickness is favorable to keep the coated particles stable physically and magnetically. Using this method, the surface modification of core-shell composites becomes convenient.

In the magnetic core-shell  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , amorphous silica shells have surfaces decorated with hydroxyl group that renders intrinsically hydrophilic. The hydrophilic surfaces easily adhere to each other through hydrogen bonding and form irregular agglomerations. In order to decrease these agglomerations of particles, the surface of the silica shell modifies with the coupling agents. The modification process is described as a hydrolysis and a condensation reaction between the coupling agents and the silica shell. Consequently, the surface modification

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removes the silanol groups on the surface of the core-shell particles and changes the hydrophilic surface into a hydrophobic one. The aim of this study is to modify the surface of  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$  core-shell microsphere by vinyltriethoxysilane (VTES) in order to remove the silanol groups on the  $\text{SiO}_2$  shell and decrease the agglomerations of this sample in its applications.

## Methods

### Materials

Ammonium hydroxide (25 wt%  $\text{NH}_3$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), hydrochloric

acid (HCl), tetraethylorthosilicate (TEOS), and VTES were supplied from Sigma-Aldrich (MO, USA). Ferric sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hydroxide (NaOH), deionized water, and cetyltrimethylammonium bromide (CTAB) were prepared from Merck & Co., Inc. (NJ, USA).

### Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles

In this work,  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by coprecipitation method. At first, 0.04 mol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 0.02 mol of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in 50 ml of 0.5 M HCl solution. Then, 500 ml of 1.5 M NaOH was added dropwise to the solution under vigorous stirring at  $80^\circ\text{C}$ . The obtained  $\text{Fe}_3\text{O}_4$  precipitant was separated with a magnet and was repeatedly washed with deionized water. Finally, the precipitant was dried at  $50^\circ\text{C}$  for 4 h [17]. The chemical reaction of  $\text{Fe}_3\text{O}_4$  precipitation is expected as follows (Equation 1):



### Synthesis of $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ core-shell microspheres

$\text{Fe}_3\text{O}_4@ \text{SiO}_2$  core-shell microspheres were prepared through the hydrolysis of TEOS, using sol-gel process. The details were as follows: 0.50 g  $\text{Fe}_3\text{O}_4$  nanoparticles was added in 50 ml of 0.1 M HCl aqueous solution, and the mixture was subjected to ultrasonic treatment for 10 min. Then, the precipitant was separated with a magnet and was washed with deionized water three times. The obtained precipitant was added to a mixture of 80 ml ethanol, 20 ml deionized water, 2.0 ml ammonia solution (25 wt %), and 0.2 ml TEOS. The resulting mixture was stirred for 6 h at room temperature. Then, the precipitant was separated with a magnet and was washed with deionized water three times. The obtained precipitant was dispersed in a mixture of 80 ml ethanol, 60 ml deionized water,

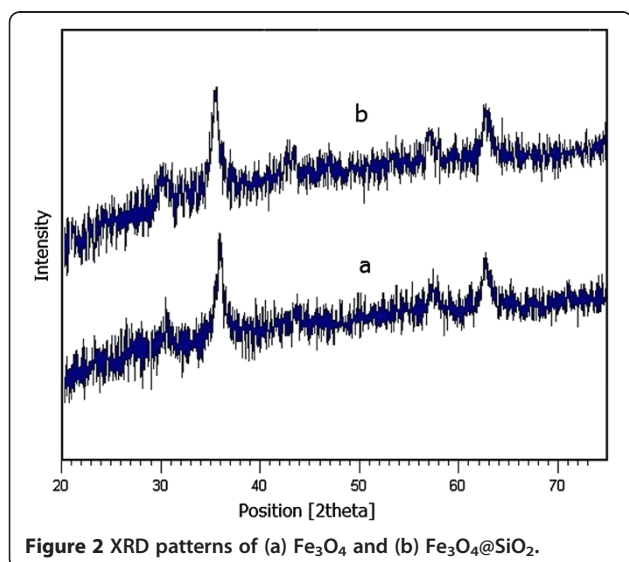


Figure 2 XRD patterns of (a)  $\text{Fe}_3\text{O}_4$  and (b)  $\text{Fe}_3\text{O}_4@ \text{SiO}_2$ .

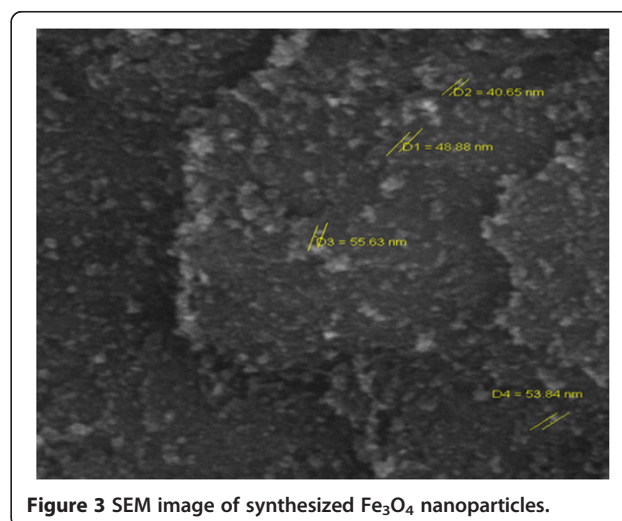
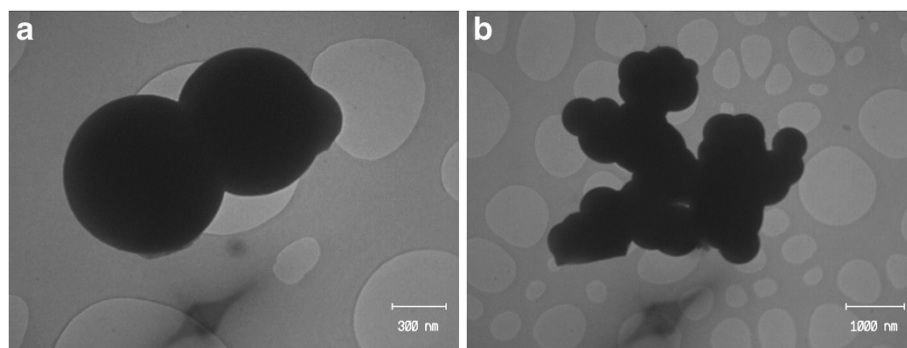


Figure 3 SEM image of synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles.



**Figure 4** TEM images of the synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres.

2.0 ml ammonia solutions (25 wt%), and 0.50 g of CTAB. The reaction mixture was stirred for 1 h; then, 1.0 ml TEOS was added. After stirring for 6 h, the resulting  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  precipitant was separated with a magnet and was washed with deionized water and ethanol. Finally, the precipitant was dried at  $50^\circ\text{C}$  for 12 h [18].

#### Surface modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ core-shell microspheres

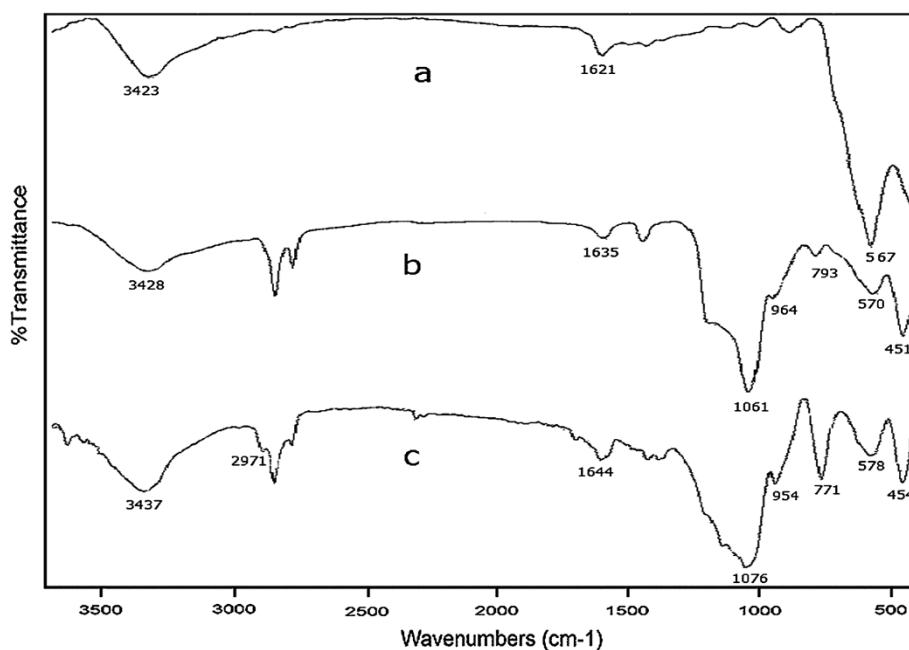
The VTES as silane coupling agent was used to covalently couple with the silica surface of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres. At first, 0.1 g  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres was added in a mixture of 26.6 ml ethanol and 6.6 ml deionized water; then, 1.76 ml VTES was added to this mixture. After subjecting the mixture to ultrasonic treatment for 30 min, 3  $\mu\text{l}$  ammonia solution (25 wt%) was dripped into the reaction mixture, and the solution was shaken for 2 h at room temperature. The solution

was heated for 1 h at  $50^\circ\text{C}$ . At the end, the modified  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  precipitant was separated with a magnet and was washed with ethanol three times in order to remove the excessive coupling agent. The resulting precipitant was dried at room temperature. The overall schematic is presented in Figure 1.

#### Results and discussion

##### X-ray diffraction

The X-ray diffraction (XRD) patterns of (a)  $\text{Fe}_3\text{O}_4$  and (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  are shown in Figure 2. In Figure 2 curve a, weak diffraction peaks with  $2\theta$  at  $30.0^\circ$ ,  $35.6^\circ$ ,  $48.3^\circ$ ,  $57.2^\circ$ , and  $62.5^\circ$  are observed, which indicate that the  $\text{Fe}_3\text{O}_4$  particles have an amorphous structure. From Figure 2 curve b, we can observe that the XRD pattern of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres is similar to the pattern of  $\text{Fe}_3\text{O}_4$  nanoparticles because the coating of the  $\text{SiO}_2$



**Figure 5** FTIR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and (c) modified  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  by VTES.

layer does not change the structure of the  $\text{Fe}_3\text{O}_4$  nanoparticles [19].

#### Scanning electron microscopy

To determine the morphology and the average size of  $\text{Fe}_3\text{O}_4$  particles, scanning electron microscopy (SEM) was used. In Figure 3, the SEM image of the  $\text{Fe}_3\text{O}_4$  particles shows that these particles have an irregular morphology, and the average size is about 50 nm.

#### Transmission electron microscopy

Figure 4 shows the transmission electron microscopy (TEM) images of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres. We can clearly see that the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  particles are spherical with a smooth surface. The average particle size is about 500 nm, and it was because of the agglomeration of  $\text{Fe}_3\text{O}_4$  inside the microspheres and the surface growth of  $\text{SiO}_2$  on the shell [20]. The internal structure cannot be clearly seen due to the larger particle size of the microspheres, which cannot be broken down by electron beam from transmission electron microscopy [18].

#### Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$ , and (c)  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  modified by VTES are shown in Figure 5. In all curves in Figure 5, the bands at around 1,621 and 3,423  $\text{cm}^{-1}$  can be assigned to the H-O-H stretching modes and bending vibration of the free or adsorbed water, respectively.

In Figure 5 curve a, the band at 567  $\text{cm}^{-1}$  is related to the Fe-O bending vibration. In Figure 5 curve b, the broad high-intensity band at 1,061  $\text{cm}^{-1}$  is associated with the motion of oxygen in Si-O-Si antisymmetric stretch, due to the asymmetric stretching bonds of Si-O-Si in  $\text{SiO}_2$ . The band at 793  $\text{cm}^{-1}$  is assigned to the Si-O-Si symmetric stretch, while the band at 451  $\text{cm}^{-1}$  corresponds to the Si-O-Si or O-Si-O bending modes. The band at 964  $\text{cm}^{-1}$  is assigned to the Si-O symmetric stretch. The band at 570  $\text{cm}^{-1}$  is an indication of the presence of Si-O-Fe. In Figure 5 curve c, the broad band at 1,076  $\text{cm}^{-1}$  is for asymmetric stretching bonds of Si-O-Si, the band at 771  $\text{cm}^{-1}$  is for Si-O-Si symmetric stretch, the band at 454  $\text{cm}^{-1}$  is for Si-O-Si or O-Si-O bending modes, the band at 954  $\text{cm}^{-1}$  is for Si-O symmetric stretch, and the band at 578  $\text{cm}^{-1}$  is for Si-O-Fe. The C=C band cannot be seen in the Figure 5 curve c because it appears at around 1,640  $\text{cm}^{-1}$ , and it overlaps with the O-H stretching vibration of  $\text{H}_2\text{O}$ . The absorption band at 2,971  $\text{cm}^{-1}$  is associated with the C-H of vinyl groups. These results show that the surface modification of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  by VTES was successful.

#### Conclusions

The  $\text{Fe}_3\text{O}_4$  nanoparticles were prepared by co-precipitation from  $\text{Fe}^{+3}$  and  $\text{Fe}^{+2}$ , and silica particles were coated on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles through the hydrolysis of TEOS in a sol-gel process. The characterization results of SEM and TEM showed that the average diameters of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  were about 50 and 500 nm, respectively. The analysis of the XRD patterns showed that the structures of these samples were amorphous. In the FTIR spectra, we showed that the chemical bonds of Fe-O-Si happened at the surface of the  $\text{Fe}_3\text{O}_4$  nanoparticles. Also, VTES was covalently coupled with the silica surface of the  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  microspheres. Consequently, it was proved that the surface modification happened. Surface chemical modification is one of the various methods to enhance the compatibility between the hydrophobic polymer and the hydrophilic fillers [21,22]. Therefore, the hydrophobic surface of  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-Si-CH=CH}_2$  microspheres will be advantageous to be used as the filler in polymeric materials.

#### Competing interests

The authors declare that they have no competing interests.

#### Authors' contributions

FA prepared the samples, the characterized of the results, and prepared the manuscript. AH and SN carried out the characterization and the interpretation of the results. All authors read and approved the final manuscript.

#### Authors' information

FA is a MSc student of Applied Chemistry. AH is an associate professor of Physical Chemistry, SN is an associate professor of Applied Chemistry.

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